5

PROCESS FOR THE PREPARATION OF MIDDLE DISTILLATES AND LUBE

BASES STARTING FROM SYNTHETIC HYDROCARBON FEEDSTOCKS.

The present invention relates to a process for the

10   preparation of middle distillates and lubricating bases

starting from prevalently paraffinic hydrocarbon feedstocks

of a synthetic origin.

More specifically, the present invention relates to a

process for the contemporaneous production of middle dis-

15   tillates and lubricating bases, with a balanced yield,

starting from feedstocks mainly consisting of n-paraffin

mixtures, comprising at least one hydrocracking step in the

presence of a particular bi-functional catalyst.

Mixtures of prevalently paraffinic hydrocarbons, in-

20   cluding a considerable fraction with a high boiling point,

are normally obtained as distillation residues in the re-

fining processes of fuels of a petroleum origin. Other

mainly paraffinic products are, for example, so-called

"slack waxes" which are obtained as by-product of the pro-

25   duction of lubricating bases through a solvent extraction

process.

The production is also known, of hydrocarbon mixtures essentially consisting of n-paraffins, wherein a significant fraction has a boiling point of over 370°C, through
5 catalytic synthesis, from mixtures of hydrogen and carbon monoxide (synthesis gas), in so-called Fischer-Tropsch processes, from the name of the inventors of the first synthesis of this type in the thirties'.

It is known that the Fischer-Tropsch (FT) synthesis
10 leads to the formation of products consisting of n-paraffins (>90%), in addition to lower percentages of alcohols and olefins, characterized by a wide range of molecular weights. These products are normally in solid or semi-solid (waxes) form at room temperature. A characteristic of
15 the FT process is that it is impossible to synthesize a product with a narrow molecular weight distribution. Moreover, due to the chemical nature of the products, the low temperature characteristics of the middle distillate cut are very poor.

20   For the above reasons, it is necessary to subject said hydrocarbon mixtures, especially FT waxes, to degradation and/or regradation treatment to obtain products of greater interest, such as fuels, lubricants, solvents and other derivatives having better properties. At present, an improve-
25 ment in the above-mentioned aspects is obtained by subject-

ing the waxes to more or less complex processes for the re-
duction of the chain length in the presence of hydrogen
(usually known by term "hydrocracking") and hydro-
isomerization.

5   The kerosene and gas oil produced through the hy-
drocracking of FT waxes, have excellent characteristics
both for specific requests as fuel and also due to their
low environmental impact. The absence of heteroatoms, such
as sulphur, and aromatic structures, leads to a drastic re-
10   duction in polluting emissions such as particulate and NO_x.

At the same time, other hydrocracking and/or isomeri-
zation catalysts have been developed for the production of
lubricating oils, having optimum performances in terms of
composition and isomerization degree of the lubricating
15   bases obtained starting from n-paraffin feedstocks. These
hydrocracking processes are carried out in the presence of
a bi-functional catalyst, containing a metal with a hydro-
dehydrogenating activity supported on an inorganic solid
normally consisting of an oxide or silicate with acidic
20   characteristics.

Hydrocracking catalysts typically include metals of
groups 6 to 10 of the periodic table of elements (in the
form approved by IUPAC and published by CRC Press Inc. in
1989, to which reference will be made hereunder), espe-
25   cially nickel, cobalt, molybdenum, tungsten or noble metals

such as palladium or platinum. Whereas the former are more suitable for processing hydrocarbon mixtures having relatively high sulphur contents, noble metals are more active but are poisoned by sulphur and require a feedstock which

5   is essentially without this.

Supports which can be used for the purpose are various type of zeolites (β, Y), X-Al$_2$O$_3$ (where X can be Cl or F), silico-aluminas, the latter being amorphous or with various crystallinity degrees, or mixtures of crystalline zeolites

10   and amorphous oxides. A very wide examination of the different catalysts, the specific characteristics and different hydrocracking processes based on the same, can be found, among the many available in literature, in the publication of J. Scherzer and A. J. Gruia "Hydrocracking Sci-

15   ence and Technology", Marcel Dekker, Inc. Editor (1996).

It is also well known that the above-mentioned isomerization and hydrocracking processes are carried out under conditions wherein the conversion per passage of the high boiling fraction is rarely over 90% and is normally

20   maintained at below 80%, especially to reduce the production of low value light fractions. The non-converted fraction can be recycled to the hydrocracking, or is separated and used for the production of lubricating bases. In this case, it is necessary for the high-boiling residue to be

25   subjected to further treatment (isomerization and/or dewax-

ing) whose purpose is to transform or separate the waxy fraction present therein.

One of the most relevant problems in the hydrocracking process of linear paraffin mixtures, consists of the diffi-

5   culty of contemporaneously obtaining, from the same proc-
ess, middle distillates with good low temperature charac-
teristics and a 360+ °C fraction with suitable characteris-
tics in terms of average molecular weight and isomerization
degree, for the production of bases for lubricant oils. If

10 a 150+ °C cut is subjected to hydrocracking using the cata-
lytic systems currently in use and the reaction is carried
out so as to obtain middle distillates having good low tem-
perature characteristics, the 360+ °C residue has too low a
molecular weight and consequently the obtained lubricating

15 base exhibit a low viscosity. When the reaction, on the
contrary, is carried out so as to obtain a 360+ cut with a
sufficiently high molecular weight, the yields of lubricat-
ing base are low, due to the presence of a still high quan-
tity of linear paraffins, which makes it necessary a subse-

20 quent dewaxing step and, in addition, the cold properties
of the middle distillates are not satisfactory.

No solution seems to have been found as yet for the above overall problems with respect to the processes and catalysts of the known art. Even though the use, as cata-

25 lyst support, of certain particular amorphous micro-meso-

porous silico-aluminas, as described in European patent application EP-A 1,101,813, is capable of providing an excellent equilibrium between gas oil and kerosene in the middle distillate fraction, it apparently does not also allow a

5 fraction of lubricating base to be produced with optimal characteristics which enable it to be adopted without any further specific treatment.

It has now been surprisingly found that certain amorphous silico-aluminas with a low aluminum content, contain-

10 ing certain quantities of phosphorus, bonded to the oxide matrix, are advantageously suitable as active support in combination with one or more metals with a hydro-dehydrogenating function, for the preparation of a catalyst for refining processes such as the hydro-treatment of hy-

15 drocarbons for the production of fuels and lubricating bases.

A first object of the present invention therefore relates to a process for the preparation of middle distillates and lubricating bases starting from a mix of mainly

20 paraffinic hydrocarbons obtained by means of a synthesis process from hydrogen and carbon monoxide, consisting for at least 30%, preferably at least 50%, of a high-boiling fraction with a distillation temperature higher than 360°C, comprising:

25 (i) at least one hydrocracking step, wherein said hydro-

carbon mix is reacted with hydrogen at a temperature of between 200 and 450°C and a pressure of between 0.5 and 15 MPa, in the presence of a catalyst, for a time sufficient for converting at least 40%, preferably from 60 to 95%, of

5   said high-boiling mix, into a fraction of hydrocarbons which can be distilled at temperatures lower than 360°C;

(ii) at least one distillation step of the product of step (i) for separating at least a fraction of middle distillate and at least one residue with a boiling point higher than

10   340°C, used, at least partially, for the preparation of a lubricating base;

characterized in that the catalyst in said hydrocracking step (i), includes a solid supported catalyst comprising:

(A) a support of an acidic nature consisting of a catalyti-

15   cally active porous solid, including silicon, aluminum, phosphorus and oxygen bonded to one another in such a way as to form a mixed amorphous solid forming a single phase, characterized by an Si/Al atomic ratio of between 15 and 250, a P/Al ratio of at least 0.1, but lower than 5, pref-

20   erably of between 0.3 and 3.5, a total pore volume ranging from 0.5 to 2.0 ml/g, an average pore diameter ranging from 3 nm to 40 nm, and a specific surface area ranging from 200 to 1000 m^2/g, preferably between 300 and 900 m^2/g;

(B) at least one metal with a hydro-dehydrogenating activ-

25   ity selected from groups 6 to 10 of the periodic table of

elements, dispersed on said support (A) in an amount of between 0.05 and 5% by weight with respect to the total weight of the catalyst.

Other objects of the present invention will ap-
5   pear evident from the following description and claims.

The meaning of some of the terms used herein is defined hereunder, for the purpose of clarifying the description and claims of the present patent application and defining its scope:

10 -   the term amorphous as used herein with reference to the porous support of the catalyst of the present invention and its compositions and uses, indicates a substantial absence of low angle X-ray scattering signals, according to the usual measuring technique described further on;

15 -   "distillation temperature" referring to a hydrocarbon mix, indicates, when not otherwise specified, the head temperature or temperature range of a typical distillation column wherein said mixture is collected, at normal pressure (0.1009 MPa);

20 -   the range definitions always include the extremes, when not otherwise specified, nevertheless, the term "range included" within two extremes, refers to any range between said extremes;

-      the term "hydrocracking" is used herein with the general meaning of the high temperature catalytic treatment of

25

a hydrocarbon mix, preferably including a fraction with a boiling point higher than 350°C, in the presence of hydrogen, obtaining a mixture with a lower boiling point; the hydrocracking treatment normally also includes so-called

5   hydro-isomerization treatment, in so far as an isomerized product is obtained, having a boiling temperature lower than that of the feeding mix;

- the terms "kerosene" and "gas oil" as hereinafter used, refer to the two hydrocarbon fractions forming the

10   so-called middle distillate, with a distillation temperature of between 140 and 280°C and between 240 and 380°C, respectively.

In its most general form, the acidic support (A) of the catalyst, according to the present invention, essen-

15   tially comprises an amorphous homogeneous phase of mixed silicon, aluminum and phosphorus oxide, wherein the phosphorus is in the maximum oxidation state (+5) and is commonly bonded to the matrix of the other oxides by means of P-O-Al bonds, as determined by means of ^{27}Al-NMR and ^{31}P-NMR

20   spectroscopic analysis. It has an extremely high surface area (determined by the BET method), preferably ranging from 300 to 900 m^2/g, more preferably from 400 to 800 m^2/g, and a pore size within the range of mesopores, preferably with an average diameter (determined by means of the DFT

25   method) ranging from 5 to 30 nm, more preferably from 6 to

25 nm. The porosity (total pore volume as ml/g) is ex-
tremely high and can be regulated, within certain limits,
through the times, temperatures and other operating parame-
ters during the gel formation in the preparation process of
5   said support. The porosity of the amorphous support pref-
erably ranges from 0.7 to 1.7 ml/g.

From a morphological point of view, the catalytically
active amorphous solid of the present invention comprises a
non-ordered network of pores with an essentially monomodal
10   size distribution within a relative wide range. The differ-
ence between 10% and 90% of the pore dimensions in the dis-
tribution curve is preferably within a range of diameters
from 2 to 40 nm, preferably from 5 to 30 nm. The oxides
forming the matrix are in turn arranged disorderly in a
15   three-dimensional polymeric lattice, without forming crys-
talline structures detectable with X-rays.

Said acidic amorphous support prevalently consists of
silicon oxide and is characterized by the presence of cer-
tain quantities of Al and P homogeneously bonded and dis-
20   tributed in the oxide matrix, so that the P/Al ratio is
lower than 5 and at least equal to 0.1. For P/Al ratio val-
ues of 5 or higher, a substantial collapse of the porous
structure is observed, with a considerable decrease in the
catalytic and support properties; for P/Al values lower
25   than 0.1, no substantial progress was observed with respect

to a traditional amorphous silica and alumina matrix having an analogous composition. More advantageous results were obtained when the P/Al ratio ranges from 0.3 to 3.5, and particularly within the range of 0.5 to 2.5.

5   One of the essential characteristics of the catalyst of the present invention is the selection in the support (A) of the aluminum content within a narrow and quantitatively limited range, which in turn determines the phosphorus content range. The Si/Al atomic ratio preferably ranges

10   from 20 to 200, more preferably from 25 to 150.

Said amorphous support can also comprise, when necessary, smaller quantities of other components, in a mix or dispersed in the oxide matrix, in particular other metal compounds, especially oxides, different from those forming

15   the component (B), suitable for giving particular characteristics or catalytic functions. Said additional components do not normally form more then 20% by weight of the amorphous solid, preferably up to 10% by weight. In particular, the catalyst support according to the present in-

20   vention can contain, in a mixture, phosphorus oxides or phosphates not bonded to the matrix of amorphous silica and alumina. Other oxides which can be present are those of certain transition metals, particularly selected from Ti, Zr, V, Zn, Ga and Sn, whereas alkaline or alkaline earth

25   metals are preferably absent or only present in traces.

These metals can advantageously provide the amorphous solid of the present invention with improved mechanical properties and further catalytic functions, such as oxidation, which are requested for certain industrial processes.

5   Said amorphous support can be prepared by adapting various typical sol-gel methods for the preparation of micro- or meso-porous amorphous silico-alumina, by the addition of a suitable quantity of an appropriate phosphorus compound in any of the steps preceding calcination, pref-

10   erably before or during the formation of gel. The phosphorus compound is preferably selected form organic or inorganic oxygenated compounds, capable of forming phosphorus oxide or a phosphate group after the oxidizing thermal treatment suitable for drying and calcining the gel, more

15   preferably such as to avoid introducing traces of undesirable metals in the matrix of porous oxide obtained after calcination.

Sol-gel methods for the preparation of amorphous silico-aluminas which can be adapted for the purpose, are

20   described, for example, in European patent applications EP-A 160,145, EP-A 340,868 and EP-A 659,478 or in the publication "Journal of Catalysis, Vol. 60 (1969), pages 156-166, whose contents are incorporated herein as reference, without out limiting the scope of the present invention to said

25   methods.

An advantageous preparation method of said amorphous active support (A), includes, in a first step, the preparation of a mixture comprising a tetra-alkyl ammonium hydroxide, an aluminum compound and a silicon compound, which can

5   be hydrolyzed to the corresponding oxide hydrates, an oxygenated compound of phosphorus and a sufficient quantity of water to dissolve and hydrolyze said compounds, wherein said tetra-alkyl ammonium hydroxide comprises from 1 to 10 carbon atoms in each alkyl residue, said hydrolysable alu-

10   minum compound is preferably an aluminum trialkoxide comprising from 1 to 10 carbon atoms in each alkoxide residue, said hydrolysable silicon compound is a silicate of at least one hydrocarbon residue, preferably a tetra-alkyl ortho-silicate, comprising 1 to 10 carbon atoms for each al-

15   kyl residue, and said oxygenated phosphorus compound is a salt or phosphate or phosphonic ester or the corresponding acid, preferably an ammonium salt or a phosphate or phosphonic ester in which each alkyl residue comprises from 1 to 10 carbon atoms.

20   The aqueous mixture of the above compounds is then hydrolyzed and gelled in a second step, by heating in an alkaline environment, preferably at a pH greater than 10, either by refluxing in a closed vessel, at the normal boiling point or higher, or in an open vessel below this tempera-

25   ture, so that there is essentially no exchange of material

with the outside. The gel thus produced is subsequently subjected to a third drying and calcination step.

The aqueous mixture in said first step can be made up in water or in a mixture of water and a soluble oxygenated

5   organic compound, preferably an alcohol having from 1 to 10 carbon atoms, in a quantity of up to 1/1 in moles with respect to the water. More preferably, the oxygenated compound is an alcohol having from 2 to 5 carbon atoms. During the hydrolysis, a further quantity of alcohol is released

10   into the aqueous solvent.

The tetra-alkyl ammonium hydroxide which can be used for the purposes of the present invention is selected, for example, from tetra-ethyl, propyl-, isopropyl-, butyl-, isobutyl-, terbutyl, and pentyl-ammonium hydroxide and

15   among these tetra-propyl-, tetra-isopropyl- and tetra-butyl ammonium hydroxide are preferred. The aluminum trialkoxide is selected, for example, from aluminum triethoxide, propoxide, iso-propoxide, butoxide, iso-butoxide and terbutoxide and among these aluminum tri-propoxide and tri-

20   iso-propoxide are preferred. The tetra-alkyl orthosilicate is selected for example from tetra-methyl-, tetra-ethyl-, propyl-, isopropyl-, butyl-, isobutyl-, terbutyl-, and pentyl-orthosilicate and among these tetra-ethyl orthosilicate is preferred.

25   The oxygenated phosphorus compound is preferably se-

lected from organic or inorganic compounds soluble in the reaction mixture, comprising a phosphate, phosphite or phosphonic group. According to an embodiment of the present invention, the phosphorus compound can also be formed in situ in the reaction mixture, or it can be added to said mixture in the form of a solution in a suitable solvent, preferably an alcohol or water. Typical phosphorus compounds suitable for the purpose are, for example, phosphoric acid, phosphorous acid, ammonium phosphate, quaternary ammonium phosphates with organic amines having from 1 to 5 carbon atoms for each residue bonded to the nitrogen atom, organic phosphites and phosphates of alcohols having from 1 to 10, preferably from 1 to 5 carbon atoms, acid phosphates of ammonium or quaternary ammonium, alkyl-phosphonates or alkyl-phosphinates of alkyl residues having from 1 to 10, preferably from 1 to 5, carbon atoms.

Particularly preferred phosphorus compounds are ammonium phosphate, acidic ammonium phosphate and the corresponding quaternary phosphates with organic amines having from 1 to 4 carbon atoms per residue, especially in the form of a solution prepared by the addition in water of phosphoric acid and the corresponding stoichiometric quantity of ammonia or amine.

In the preparation of the aqueous mixture of said first step, the order of addition of the various reagents

is not particularly critical. The phosphorus compound can
be added or formed in situ initially, together with the ad-
dition of the tetra-alkyl ammonium hydroxide, by regulating
the quantities so as to respect the desired final ratios

5   between atoms and components, or it can be added after the
introduction of the Si and Al compounds. The mixture is
prepared at room temperature or a slightly higher value,
preferably between 30 and 80°C. Although the thus formed
mixture preferably consists of a limpid solution, certain

10   compounds, such as aluminum alkoxide for example, can re-
main partially undissolved, but are completely dissolved in
the heating step and hydrolysis of the subsequent step. In
certain cases, a time of up to five hours under stirring
may be necessary for obtaining a solution.

15   In a preferred embodiment of the process for the
preparation of said amorphous solid according to the pres-
ent invention, an aqueous solution is first prepared, con-
taining the tetra-alkyl ammonium hydroxide and the aluminum
trialkoxide, operating at a temperature which is sufficient

20   to guarantee an effective dissolution of the aluminum com-
pound, preferably from 40 to 80°C. The tetra-alkyl ortho-
silicate is added to said aqueous solution. If necessary,
the pH is regulated to a value greater than 10, preferably
between 11 and 12. This mixture is brought to a tempera-

25   ture which is suitable for triggering the hydrolysis reac-

tion. Said temperature is in relation to the composition of the reaction mixture (normally from 60 to 120°C). The hydrolysis reaction is exothermic and therefore guarantees self-maintenance, once the reaction has been activated. The

5   quantities of constituents of the mixture are selected so as to respect the atomic ratios between the elements to be obtained in the catalytically active solid at the end of the preparation; the following atomic or molar ratios are conveniently used: Si/Al from 10/1 to 250/1, (tetra-alkyl

10 ammonium hydroxide)/Si from 0.05/1 to 0.2/1, H_2O/SiO_2 from 5/1 to 40/1, P/Al from 0.1 to 5.0. The preferred values for these ratios are: Si/Al from 30/1 to 150/1, (tetra-alkyl ammonium hydroxide)/Si from 0.05/1 to 0.2/1, P/Al from 0.5 to 3.5 and H_2O/SiO_2 from 10/1 to 25/1.

15   The hydrolysis of the reagents and their gelation are preferably effected operating at a temperature equal to or higher than the boiling temperature, at atmospheric pressure, of any alcohol which develops as by-product of said hydrolysis reaction, without eliminating or substantially

20 eliminating said alcohols from the reaction environment. The hydrolysis and gelation temperature is therefore critical, and is conveniently maintained at values higher than about 65°C up to about 110°C. Furthermore, in order to maintain the alcohol which was developed, within the reac-

25 tion environment, it is possible to operate in an autoclave

at the autogenous pressure of the system at the pre-
selected temperature (normally in the order of 0.11-0.15
MPa absolute), or at atmospheric pressure in a reactor
equipped with a reflux condenser.

5　　　　According to a particular embodiment of the process,
the hydrolysis and gelation are carried out in the presence
of a quantity of alcohol higher than that which develops as
by-product. For this purpose, a free alcohol, preferably
ethanol, is added to the reaction mixture in a quantity up
10　to a maximum molar ratio between alcohol added and SiO_2 of
8/1.

The time necessary for completing the hydrolysis and
gelation, under the conditions indicated above, usually
varies from 10 minutes to 3 hours and is preferably in the
15　order of 1-2 hours.

It has also been found useful to subject the gel thus
formed to aging, by maintaining the reaction mixture in the
presence of the alcohol and at room temperature, for a pe-
riod in the order of 1-24 hours.

20　　　The alcohol is finally removed from the gel which is
dried, operating according to the known art, so as to avoid
fracturing of the solid and substantially maintaining the
pore structure unaltered. Reduced pressure is normally ap-
plied, generally from 1 to 20 kPa and preferably from 3 to
25　6 kPa, together with a temperature ranging from 50 to

120°C, preferably from 100 to 110°C. According to a pre-
ferred method, the drying is effected operating with a gra-
dient (or profile) of (increasing) temperatures and (de-
creasing) pressures within the above ranges to allow the
5   gradual evaporation of the solvent. The dried gel is fi-
nally subjected to calcination in an oxidizing atmosphere
(normally in air), at a temperature ranging from 500 to
700°C for a period of 4-20 hours and preferably from 500-
600°C for 6-10 hours, also in this case preferably operat-
10   ing with a suitable temperature gradient.

The amorphous support based on silicon, aluminum and
phosphorus, thus obtained, has a composition corresponding
to that of the reagents used, considering that the reaction
yields are practically complete. Therefore, the Si/Al
15   atomic ratio varies from 15/1 to 250/1 in the preferred
case, the most preferred values ranging from 20/1 to 150/1
and specifically in the order of 100/1. This support re-
sults substantially amorphous, when subjected to analysis
by means of powder X-ray diffraction, it has a surface area
20   of at least 200 m^2/g and normally within the range of 300-
900 m^2/g and a pore volume of between 0.5-2.0 cm^3/g, pref-
erably of between 0.6 and 1.8 cm^3/g.

According to what is known in the art with respect to
heterogeneous catalysis, the above-mentioned amorphous sup-
25   port (A) of the present invention catalyst, can be advanta-

geously mixed and processes with other inert compounds such
as, for example, pseudo-bohemite which, after calcination,
becomes γ-alumina, suitable for providing enhanced mechani-
cal and morphological properties, desirable for industrial

5   use, especially for improving the consistency and stability
of the granules in the catalytic beds, thus increasing the
durability, and for reducing the amounts of catalyst resi-
dues in the product obtained. The incorporation of said in-
ert component, commonly called "binder", into the catalyst

10   support, can be effected both by addition to the amorphous
support (A) in the form of gel, or after drying or calcina-
tion, and by addition to the preformed catalyst, including
the metal (B). The addition to the support is, in any case,
preferred for the purposes of the present invention.

15   Therefore, in accordance with a particular aspect of
the present invention, said support (A) can, when neces-
sary, form a composition mixed with a suitable quantity of
a binder consisting of an inert inorganic solid, generally
added for the purpose of improving the mechanical proper-

20   ties, such as for example, silica, alumina, clay, titanium
oxide (TiO_2) or zirconium oxide (ZrO_2), boron oxide (B_2O_3)
or mixtures thereof. It is generally preferably, in fact,
for its industrial applications, for said solid to be used
in granular rather than powder form, and for it to have a

25   relatively narrow particle-size distribution. Furthermore,

it is preferably endowed with sufficient mechanical resis-
tance to compression and impact to avoid its progressive
breakage during use, due to the fluid-dynamic and vibra-
tional stress effected by the process fluids.

5   Possible binders can be all those which are known to
be suitable for the purpose, both natural and synthetic,
preferably silica and alumina, and particularly alumina in
all its known forms, for example gamma-alumina.

Said reinforced amorphous solid according to the pres-
10   ent invention can be obtained by means of any of the mix-
ing, extrusion and granulation (pelletizing) methods of
solid materials in a mixture, for example, according to the
methods described in European patent applications EP-A
550,922 and EP-A 665,055, the latter preferred, both filed
15   by the Applicant, whose contents are incorporated herein as
reference.

In particular, according to a preferred method, the
gel obtained from the hydrolysis and gelation of the aque-
ous mixture of Al alkoxide, tetra-alkyl silicate and oxy-
20   genated phosphorus compound, prepared as described above,
is mixed, before the calcination step (iii), with the de-
sired quantity of inorganic binder, based on the dry
weight, normally with a weight ratio between binder and gel
(humid) within the range of 0.05 to 0.5. A plasticizer, se-
25   lected from those generally known to be suitable for the

purpose, is also preferably added, for example methyl cel-
lulose, stearine, glycerol, more preferably methyl cellu-
lose, to favour the formation of a homogeneous mixture
which can be easily processed. This plasticizer is gener-
5   ally added in a quantity ranging from 5 to 20 g per 100 g
of binder.

A suitable acidifying compound, selected from organic
acids, such as acetic acid or acetic anhydride, oxalic
acid, or inorganic acids, such as hydrochloric acid or
10 phosphoric acid, is then added in a quantity preferably
ranging from 0.5 to 8 g per 100 g of binder. Acetic acid is
particularly preferred.

The mixture thus obtained is homogenized by mixing and
heating to a temperature ranging from 40 to 90°C, with par-
15 tial evaporation of the solvent, until a paste is obtained,
which is then extruded using suitable equipment. The ex-
truded product is cut into cylindrical granules, preferably
with a size of 2-10 mm in length and 0.5-4.0 mm in diame-
ter. According to an alternative embodiment, the above ho-
20 mogeneous paste can also be dried in a suitable granulator,
in order to obtain granules having the desired dimensions.

The granules thus obtained are subjected to progres-
sive heating to eliminate the residual quantities of sol-
vent and finally calcined in an oxidizing atmosphere, gen-
25 erally in a stream of air, at a temperature ranging from

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400 to 600°C, for 4-20, preferably 6-12 hours.

A granular acid solid is thus obtained, having the de-
sired catalytic and mechanical properties, containing a
quantity of 1 to 70% by weight, preferably from 20 to 50%

5   by weight, of said inert inorganic binder, the remaining
percentage consisting of amorphous support (A), as previ-
ously defined. The granular solid is preferably in the form
of pellets having a size of about 2-5 mm in diameter and 2-
10 mm in length.

10   Both the porosity and surface area of the extruded
product normally have average values with respect to the
values of the single components in the mixture, according
to linear composition rules.

The catalytically active amorphous support of the pre-

15   sent invention, both as such and mixed with other inert ma-
terials, has acidic characteristics. It is distinguished by
the advantageous combination of a pore diameter and surface
area which are both relatively high. According to the stud-
ies carried out by the Owner, this combination favours a

20   particularly desirable catalysis selectivity and orienta-
tion, especially in hydro-treatment processes of hydrocar-
bons, and paraffins in particular, for example in the
transformation processes of hydrocarbon fractions, such as
hydrocracking, hydro-isomerization and dewaxing, with im-

25   proved activity and selectivity with respect to the tradi-

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tional amorphous silica-alumina gel, particularly when a range of products, from kerosene to the lubricating bases, is to be obtained, by reducing as much as possible the use of dewaxing steps, separated or subsequent to the hy-

5   drocracking step.

According to the present invention, the metal of component (B) of the catalyst is selected from those having a hydro-dehydrogenating activity, in the presence of hydrogen/hydrocarbon mixtures, under the suitable process condi-

10   tions. Metals especially suitable for the purpose are those selected from groups 6 to 10 of the periodic table. Combinations of nickel with molybdenum, tungsten and cobalt as well as the noble metals platinum or palladium, or mixtures thereof, and preferably platinum and palladium, more pref-

15   erably platinum, are of particular interest.

Combinations of metals of group 6, especially tungsten or molybdenum, with the metal of group 9, especially nickel or cobalt, are particularly suitable, as is known for other catalysts of the art suitable for processing hydrocarbons,

20   when the mixtures contain non-negligible amounts of sulphur.

According to the present invention, said catalyst can be prepared through a method which includes contact, under suitable conditions, of said active support (A) with a

25   suitable compound of said metal (B). The metal is conven-

iently distributed as uniformly as possible on the porous

surface of the support, in order to maximize the catalytic

surface which is effectively active. For this purpose,

various known methods can be used, such as those described

5   for example in European patent application EP-A 582,347,

whose contents are incorporated herein as reference. In

particular, according to the impregnation method, the amor-

phous support (A), as such or preferably extruded, is put

in contact with an aqueous and/or alcoholic solution of a

10   soluble compound of the desired metal for a period suffi-

cient to provide a homogeneous distribution of the metal in

the solid. This normally requires from a few minutes to

several hours, preferably under stirring. Soluble salts

suitable for the purpose are, for example, H_2PtF_6, H_2PtCl_6,

15   $[Pt(NH_3)_4]Cl_2$, $[Pt(NH_3)_4](OH)_2$ and analogous salts of palla-

dium; mixtures of salts also of different metals are

equally included in the scope of the invention. The minimum

quantity of aqueous liquid (normally water or an aqueous

mixture with a second inert liquid or with an acid in a

20   quantity lower than 50% by weight) is conveniently used,

which is sufficient to dissolve the salt and uniformly im-

pregnate said support, preferably with a weight ratio solu-

tion/solid ranging from 1 to 3. The quantity of metal is

selected on the basis of its concentration which is to be

25   obtained in the catalyst, as the whole metal is fixed on

the support.

At the end of the impregnation, the solution is evapo-
rated and the solid obtained is dried and calcined in an
inert or reducing atmosphere, under analogous temperature
5   and time conditions as those cited above for the calcina-
tion of the amorphous solid or extruded product.

An alternative method to impregnation is the ion ex-
change system. According to the latter, the amorphous sil-
ica/alumina/phosphate solid is put in contact with an aque-
10   ous solution of a salt of the metal as in the previous
case, but the deposition takes place by exchange under con-
ditions made basic (pH between 8.5 and 11) by the addition
of a sufficient quantity of an alkaline compound, normally
an ammonium hydroxide. The suspended solid is then sepa-
15   rated from the liquid by means of filtration or decanting
and dried and calcined as specified above.

According to another alternative, the salt of the
metal (B) can be included in the catalytically active sup-
port in the gel preparation step, for example before hy-
20   drolysis for the formation of humid gel, or before its cal-
cination.

At the end, a catalyst is obtained for the hydrotreat-
ing of hydrocarbons, in accordance with the present inven-
tion, wherein metal M is uniformly dispersed in amounts
25   ranging from 0.05 to 5% by weight, preferably from 0.1 to

2%, more preferably from 0.2 to 1% by weight, with respect to the total weight of the catalyst, especially when the metal is selected from Pt and Pd.

A typical method for the preparation of a catalyst in extruded form, comprising the active solid of the present invention as support, includes the following steps:

(a) solution A is prepared of the hydrolysable components and ammonium phosphate as described above, in suitable quantities for obtaining the desired final composition;

(b) the above solution is heated to 60-70°C to cause its hydrolysis and gelation and to obtain a gel mixture with a viscosity ranging from 0.01 to 100 Pa•sec;

(c) a binder, belonging to the group of bohemites or pseudobohemites, is first added to the gel mixture, in a weight ratio with the same ranging from 0.05 to 0.5, followed by methyl cellulose as plasticizer in a quantity ranging from 10 to 20 g per 100 g of said binder; and finally a mineral or organic acid in a quantity ranging from 0.5 to 8.0 g per 100 g of said binder;

(d) the mixture obtained under point (c) is heated under mixing to a temperature ranging from 40° to 90°C until a homogeneous paste is obtained, which is subjected to extrusion and granulation;

(e) the extruded product obtained under (d) is dried and

calcined in an oxidizing atmosphere.

In this way, a granular solid support is obtained, with an acidic catalytic activity, containing a quantity ranging from 30 to 70% by weight of inert inorganic binder, the remainder consisting of the active porous solid of silicon/aluminum/phosphorus oxide, having essentially the same characteristics of porosity, surface extension and structure as described above for the same porous solid without binder. The granules are conveniently in the form of pellets having a size of about 2-5 mm in diameter and 2-10 mm in length.

The supporting step of the noble metal on the active granular solid is effected with the same procedure specified above.

Before use, the catalyst thus obtained is normally subjected to activation in a reducing atmosphere, according to one of the known methods suitable for the purpose, which can also be carried out directly in the reactor pre-selected for the hydrocracking reaction. A typical method uses the procedure described hereunder:

1) 2 hours at room temperature in a nitrogen stream;

2) 2 hours at 50°C in a stream of hydrogen;

3) heating to 310-360°C with an increase of 3°C/min in a stream of hydrogen;

4) constant temperature of 310-360°C for 3 hours in a

stream of hydrogen and cooling to 200°C.

During the activation, the pressure in the reactor is maintained between 3.0 and 8,1 MPa (30 to 80 atms).

Using the catalyst as described above in the hydrocar-
5 bon hydrocracking process of the present invention, it was surprisingly possible to obtain, with an excellent yield, the conversion of heavy paraffin fractions (waxes with a boiling point over 360+°C) into middle distillates having good properties at low temperatures, and contemporaneously
10 produce a residue with a high content, preferably higher than 70% by weight, of lubricating base having a high vis-cosity index and a suitable viscosity especially for use for motor-vehicle engines.

The hydrocarbon mix fed to the process according to
15 the present invention, preferably consists of substantially linear synthetic paraffins, and can include a middle dis-tillate fraction in addition to the fraction of high-boiling hydrocarbons (liquid and/or solid at room tempera-ture). According to the process of the present invention,
20 the amount of low-boiling fraction (<150°C, naphtha and volatile matters) produced, even in the presence of an amount of middle distillate higher than 50% in the feeding, is normally very limited, preferably lower than 15%, also with conversion per passage of between 80 and 90%.

25 The hydrocarbon mix suitable for feeding the process

according to the present invention, can generally comprise
up to 20%, preferably up to 10% by weight, of an organic
non-paraffinic fraction. In particular, it has a reduced
sulphur content, preferably lower than 5,000 ppm by weight

5 of S, better if lower than 1,000 ppm or even non-traceable
and can contain oxygenated organic compounds, such as alco-
hols, ethers or carboxylic acids, preferably in an amount
lower than 5% by weight.

For an optimum embodiment of the process according to

10 the present invention, said feeding mix of the hydrocrack-
ing step preferably consists, for at least 80%, of linear
paraffins having from 5 to 80, preferably from 15 to 70,
even more preferably from 20 to 65 carbon atoms, and an
initial boiling point ranging between 45 and 675°C (by ex-

15 trapolation), preferably between 170 and 630°C (by extrapo-
lation).

According to a particular aspect of the present inven-
tion, said feeding to step (i) includes at least 30% by
weight, preferably from 40 to 80% by weight of a high-

20 boiling fraction distillable at a temperature ≥ 360°C, and
up to 80%, preferably from 20 to 60% by weight of a hydro-
carbon fraction corresponding to the s-called "middle dis-
tillate", divided into the traditional kerosene and gas oil
cuts, previously defined.

25 According to a different preferred aspect of the pres-

ent invention, the feeding mix has a boiling point of at least 260°C, more preferably of at least 350°C. It has been found that, under these conditions, especially if the feed consists of substantially linear hydrocarbons, it is possi-
5   ble to produce both middle distillates and lubricating bases having optimum characteristics, and in the desired relative amounts, within the limits imposed by the initial feeding composition.

Processes in which the feed is different from the pre-
10 ferred ones mentioned above, are not excluded from the present invention. The prevalently linear hydrocarbon mixtures having distillation intervals equal to or higher than 260°C, are solid or semisolid at room temperature and for this reason they are normally called waxes.

15 Typical examples of suitable feeds are mixtures of synthetic hydrocarbons prepared through processes using mixtures of hydrogen and carbon monoxide (so-called synthesis gas) as feed, for example those obtained by means of the Fischer-Tropsch process.

20 The latter are particularly characterized by the absence of sulphur and preferably consist, for over 70% by weight, of linear paraffins having more than 15 carbon atoms and a boiling point higher than 260°C. As already mentioned, these mixtures are frequently solid or semi-solid
25 at room temperature and for this reason are called waxes.

Not all Fischer-Tropsch processes provide high-boiling lin-
ear paraffin mixtures. According to the conditions and
catalyst used, the Fischer-Tropsch process can produce mix-
tures within several distillation temperature ranges, even
5   quite low, if desired. It has been found however that it is
more convenient to run the synthesis process so as to ob-
tain prevalently high-boiling mixtures or waxes, which can
be subsequently suitably degraded and fractioned into the
desired distillation cuts. It is also well known that the
10   Fischer-Tropsch synthesis provides by-products mainly con-
sisting of olefins and oxygenated products. The latter are
essentially alcohols and their concentration is lower than
10% by weight with respect to the total, if a cobalt syn-
thesis catalyst is used.

15   The hydrocracking step of the process according to the
present invention, can be generally carried out at the tem-
peratures and pressures of traditional processes of this
type, known in the art. Temperatures are normally selected
between 250 and 450°C, preferably from 300 to 370°C,
20   whereas the pressure is selected from 0.5 to 15 MPa, pref-
erably between 1 and 10 MPa, also including the hydrogen
pressure.

Hydrogen is used in a sufficient amount for effecting
the desired conversion under the selected conditions. The
25   mass ratio between hydrogen and hydrocarbons in the feeding

(and consequent relative pressure of the same) can be eas-
ily selected by technical experts, depending on the other
essential parameters of the process, such as the space ve-
locity, the contact time, the catalyst activity and tem-
5   perature, so to achieve the desired conversion degree. Ini-
tial (hydrogen)/(hydrocarbons) mass ratios of between 0.03
and 0.2 are normally considered to be satisfactory for car-
rying out the process, these values not being, however,
limitative of the present invention. Under these condi-
10   tions, only a small part of the hydrogen initially intro-
duced is consumed, the remaining part can be easily sepa-
rated and recycled using the common equipment suitable for
this purpose. Normally, the use of essentially pure hydro-
gen, which is commercially available at low cost, is pre-
15   ferred, whereas in the most general case the use of mix-
tures of hydrogen with inert gases such as, for example,
nitrogen, is not excluded.

The space velocity WHSV (defined as maximum flow rate
as g/h, divided by the weight of the catalysts in grams),
20   or the contact time (defined as the reciprocal of the space
velocity: 1/WHSV), of the reagents under the conditions of
the hydrocracking reaction, are generally selected as a
function of the characteristics of the reactor and of the
process parameters, so as to obtain the desired conversion
25   degree. It is important for the contact time to be selected

so that the α conversion degree - calculated as a mass of the 360+°C fraction in the feedstock, minus the mass of the 360+°C fraction in the products, divided by the mass of the 360+°C fraction in the charge [$\alpha = (360+_{inlet} - 360+_{outlet})/(360+_{inlet})$] - is maintained within the values over which significant undesired reactions take place, which jeopardize the production of the desired selectivity levels to middle distillate and lubricating base, for example by producing an excess of volatile products. Contact times are normally selected which allow α conversions of the high-boiling fraction (360+°C) of between 60 and 90%, more preferably between 65 and 80%.

According to a typical embodiment of the process of the present invention, a mix of hydrocarbons having the above characteristics is preheated to a temperature of between 90 and 150°C and fed in continuous, after its pre-mixing with hydrogen, to a tubular fixed bed reactor operating in "down flow". The reactor is kept at a temperature of between 300 and 360°C. The reactor pressure is maintained at between 3 and 10 MPa. The catalyst is previously activated, for example according to the typical method mentioned above, and the hydrocracking process can be subsequently effected, normally after a catalyst stabilization step (about 60-100 hours).

The feeding preferably consists of a high-boiling mix

coming from a synthesis process of the Fischer-Tropsch type, comprising 30 to 100% of waxes having a distillation point above 360°C and up to 5% of oxygenated products. In the case of a feed containing alcohols, especially when these are in amounts higher than 5% by weight, technical experts can subject the same to a preliminary treatment, before the hydrocracking step of the process according to the present invention, in order to avoid the above-mentioned drawbacks. This treatment can consist, for example, of a distillation step which removes a fraction with a cut having a temperature lower than 360°C, preferably between 260 and 360°C, in which, as is well known, the oxygenated products are normally concentrated, or subjecting the feeding mix to a selective hydrogenation step, in the presence of one of the known catalysts suitable for the purpose and under conditions which reduce conversion to products with lower boiling points, to the minimum, so as to eliminate the oxygenated groups (such as -OH, -COOH, ether, ketone or ester) and to produce non-oxygenated hydrocarbons and a small amount of water which can be possibly removed by evaporation or decanting.

According to said typical embodiment, the supported catalyst of the present invention is introduced into the reactor in granular form, preferably as a co-extruded product with a binder, for example γ-alumina, according to what

is previously described. The metal with a hydro-dehydrogenating activity is preferably palladium or platinum, particularly platinum, especially in the case of a feed obtained by means of a Fischer-Tropsch synthesis. A fixed bed is conveniently used, on which the reagent mix is passed. The contact time is selected so as to have a conversion of between 60 and 80%. The space velocity preferably ranges from 0.4 to 8 h^{-1}, more preferably from 0.5 and 4 h^{-1}

The reaction mix at the outflow of the reactor is analyzed on line, by means of one of the known techniques, for example gas chromatography, and sent to said distillation/separation step (ii), in the upper part of which the middle distillate product is obtained, whereas the high-boiling residue, suitable for the production of lubricating bases, is obtained at the tail.

The light hydrocarbon fraction (gas and naphtha) having distillation temperatures lower than 150°C, which is normally formed in amounts lower than 10% by weight of the product obtained in step (ii), is removed by distillation from the head of the column and normally destined for different uses.

In accordance with the present invention, the high-boiling residue advantageously consists of an isomerized hydrocarbon mix having a high content, preferably over 80%,

more preferably more than 90%, or even more preferably essentially consisting of a lubricating base with a high viscosity index, a low pour point, and a heat viscosity within a particularly desirable range. In particular, the lubri-

5   cating base which can be obtained with the present process has the following preferred characteristics:

-    pour point: < -18°C

-    viscosity at 100°C: > 4.0 cSt

-    Viscosity index (VI): > 135

10   -   Noack: < 15%.

When necessary, on the basis of market requests, an aliquot of said residue, preferably not more than 90%, more preferably not exceeding 50% by weight, can be advantageously recycled to the hydrocracking step to produce fur-

15   ther middle distillate. In this case, it is also possible to improve the isomerization degree by suitably regulating the recycling, as in the normal technique of hydrocracking processes.

The operative conditions and equipment for running the

20   process of the present invention can be easily set up and optimized by the average technical expert, on the basis of the present description and parameters herein defined. A particularly advantageous aspect of this process consists of the fact that it can be effected in most cases, and es-

25   pecially, by feeding a hydrocarbon mix obtained from a

Fischer-Tropsch synthesis, essentially with a single reactive step (hydrocracking), normally combined with a single separation and recycling step, downstream of the reactor, thus obtaining high commercial value products, without nec-
5   essarily resorting to other distillation and transformation combinations, with the exception of a possible mild dewaxing step on the high-boiling residue (for example 360+°C) and/or separation of the 550°C fraction from the above residue by means of vacuum distillation to isolate the de-
10   sired lubricating base.

Several obvious variations of this process can be effected by technical experts in the filed, without involving any further inventive activity.

The solid catalyst described above can be used in the
15   process according to the present invention, as such, after activation, in the hydrocracking step of the process according to the present invention. As mentioned above, however, said catalyst is preferably reinforced by the addition and mixing of a suitable amount of a binder consisting
20   of an inert inorganic solid, capable of improving the mechanical properties.

According to a particular embodiment of the present invention, suitable for the treatment of hydrocarbon mixtures containing heteroatoms, in particular S, N or O, said
25   process for the preparation of middle distillates and lu-

bricating bases comprises, before the hydrocracking step, a hydrogenating treatment, under such conditions as to not produce any substantial variation in its average molecular weight, to obtain a substantially saturated hydrocarbon
5 mix, without heteroatoms.

Mixtures of the above type can be commonly obtained by synthesis, such as, for example, paraffin mixtures produced by means of the Fischer-Tropsch synthesis, especially with cobalt-based catalysis. In particular, such a process
10 variation is advantageously used for a substantially linear hydrocarbon mix, comprising up to 20%, preferably up to 10%, by weight of a non-paraffinic organic fraction, and it is characterized by a substantial absence of sulphur. In particular, its non-paraffinic content consists of oxygen-
15 ated organic compounds, such as alcohols or ethers, usually in amounts of between 0.1 and 10%, preferably between 1.0 and 5% by weight.

The procedure for effecting said hydrogenating treat-ment is well known in the art, and does not represent a
20 particular critical point for the process of the present invention, provided the degradation of the molecular weight of the treated fraction is practically negligible, in any case never over 15% of conversion to products included in the typical cut called naphtha, having a distillation tem-
25 perature below 150°C. The hydrogenating step, in this case,

must be such that not more than 15%, preferably not more than 10% of the constituents of the feeding mix having a distillation temperature of over 150°C, is converted to products having a lower distillation temperature.

5   Typical but non-limiting reaction conditions of the hydrogenating step are: temperature within the range of 280-380°C, hydrogen pressure between 0.5 and 10 MPa, space velocity (WHSV) ranging from 0.5 to 4 h^{-1}. The hydrogen/feedstock ratio is between 200 and 2000 Nlt/kg.

10   The hydrogenation reaction is normally effected in the presence of a suitable catalyst. The latter, according to the known art, preferably includes a metal of groups 6, 8, 9 or 10 of the periodic table of elements, dispersed on a support preferably consisting of an organic oxide, such as

15 alumina, titania, silico-alumina, etc.. Preferred hydrogenation catalysts are those based on nickel, platinum or palladium, supported on alumina, silico-alumina, fluorinated alumina, with a metal concentration which, according to the type, is between 0.1 and 70%, preferably from 0.5 to

20 10% by weight.

       During the hydrogenation step, the reaction can be carried out at conditions and with a catalyst such as to obtain, when desired, a certain isomerization degree of the hydrocarbon mix, according to the known art.

25   The hydrocarbon mix thus obtained is preferably sub-

jected to a separation step, through distillation, of gas and volatile products (< 150°C) possibly present, and, even more preferably, water and/or the other inorganic products deriving from the hydrogenation.

5   According to a further embodiment of the process according to the present invention, step (i) can be preceded by a preliminary separation step of a low-boiling fraction from the feeding mix. Said preliminary step can typically include a flash separation of a mix having a final boiling

10   point of between 150 and 370°C, preferably between 260 and 360°C, which contains most of the oxygenated compounds possibly present in the case of a feeding consisting of a Fischer-Tropsch synthesis product. The low-boiling mix thus separated can be subsequently processed according to one of

15   the known techniques for obtaining middle distillates and/or fractions suitable for the production of gasoline. For example, it can be subjected to a hydrogenation step of the type previously described, followed by an isomerization step in suitable equipment in the presence of a catalyst

20   and under such conditions as to favour the isomerization reaction with respect to the cracking reaction, such as those described, for example, in European patent EP 908.231. The desired middle distillate fractions are separated from the product thus isomerized, by means of a nor-

25   mal fractionated distillation column.

The high-boiling fraction obtained in this prelimi-
nary step, forms the feeding of step (i) and is treated ac-
cording to the process of the present invention for the
production of high quality middle distillates and lubricat-
5   ing bases. According to a preferred aspect, moreover, the
subsequent step (ii) consists of a flash distillation for
the separation of a low-boiling fraction comprising the
volatile products (150-°C) and middle distillate, from the
high-boiling isomerized residue suitable for the formation
10   of the lubricating base. Said low-boiling fraction is then
joined to the product of the above isomerization step and
sent downstream to the fractionated distillation column, or
sent, at least partially, to said isomerization step, with
the purpose of further increasing the quality of the middle
15   distillate thus obtained, particularly of the kerosene
fraction.

Some possible embodiments of the process according to
the present invention are described hereunder with refer-
ence to Figures 1 and 2, without limiting in any way the
20   overall scope of the invention as claimed herein.

In particular:

Figure 1 schematically illustrates a plant for the em-
bodiment of the process according to the present invention,
comprising a hydrocracking step and a distillation step of
25   the product mix obtained;

Figure 2 schematically illustrates a particular case
of the plant of Figure 1, wherein the distillation residue
is further treated to improve its performance as lubricat-
ing base.

5   According to the plant scheme of Figure 1, a stream 1
of substantially linear and preferably sulphur-free hydro-
carbons, obtained, for example, from a Fischer-Tropsch pro-
cess, preferably of the non-shifting type, is fed to the
hydrocracking unit (HCK) of step (i) of the present process
10   together with the necessary amount of hydrogen, through
line 2.

An aliquot of residue 8 is also possibly fed to the
same unit, through line 9, coming from the subsequent sepa-
ration of the middle distillate, preferably having a boil-
15   ing point over 350°C, in a mass ratio preferably ranging
from 0 to 90%, more preferably between 10 and 30% with re-
spect to the total residue volume.

The reaction product of the hydrocracking step, con-
sisting of a hydrocarbon mix having an isomerization degree
20   (non-linear hydrocarbon mass/mixture mass) preferably over
50%, more preferably over 70%, is fed, through line 3, to a
separation step by distillation (DIST), preferably in a
suitable column running at atmospheric pressure or slightly
higher, from which the middle distillates, suitable as fu-
25   els according to the present invention, are collected by

means of line 6 (kerosene) and 7 (gas oil). From the unit
DIST in Figure 1, the following products are also obtained:
through line 4 a gaseous fraction C1-C5, of little signifi-
cance, and, through line 5, a hydrocarbon light fraction,
5   preferably having a boiling point lower than 150°C (naph-
tha), in an overall amount advantageously lower than 20% by
weight, preferably lower than 15%, with respect to the hy-
drocarbon mix fed through line 1.

According to a particularly distinct aspect of the
10   present invention, the use of the above catalyst supported
on a silico-alumino-phosphatic amorphous solid in the hy-
drocracking step (i), allows a high quality middle distil-
late fraction to be obtained, with a high yield (low pro-
duction of 150-°C volatile products), also having, in par-
15   ticular, excellent low temperature properties and a high
cetane number, together with a high-boiling residue having
a surprisingly low content of linear paraffins, which is
particularly suitable for obtaining lubricating bases, ei-
ther as such or, preferably, after dewaxing treatment with
20   advantageously reduced contact times and conversions.

A particularly preferred embodiment of the process ac-
cording to the present invention is schematically shown in
the scheme of Figure 2.

A liquid stream 11, consisting of a mix of light hy-
25   drocarbons coming from a Fischer-Tropsch synthesis process,

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also including unsaturated products (linear olefins) in a
quantity of up to 10%, preferably from 2 to 5% by weight,
and oxygenated products (mainly alcohols), in an amount of
up to 10% by weight, preferably from 2 to 7% by weight, is

5   separated in the distillation column D1 into a light frac-
tion 13 having a final boiling point lower than 380°C,
preferably between 260 and 360°C, and a heavy fraction 14,
consisting of the distillation residue. The distillation in
D1 preferably only has one step (flash) and can be substi-

10   tuted by a differentiated collection of two fractions di-
rectly from the Fischer-Tropsch synthesis reactor.

The mass ratio of the fractions 13 and 14 is prefera-
bly included within the range of 0.5 to 2.0, more prefera-
bly from 0.8 to 1.5.

15   The light fraction 13 is fed to a hydro-isomerization
(HDSM) unit. It can however represent a drawback for the
functioning of the catalysts in this step, especially in
the case of the presence of heteroatoms or unsaturated
groups, and oxygenated products in particular, said frac-

20   tion 13 is preferably fed to a hydrogenation unit (HDT) in
which it is put in contact with hydrogen (line 12) in the
presence of a suitable catalyst, under such conditions as
to minimize or nullify the hydrocracking reaction. The hy-
drogenation unit (HDT) can be produced according to the

25   known technique and preferably comprises a pressure reactor

containing a catalyst on a fixed bed, selected from those suitable for the purpose mentioned above. Typical hydrogenation catalysts suitable for the purpose comprise a hydrogenating metal such as Ni, Pd or Pt supported on an inert solid or having an acidic activity, such as alumina, silica, silico-alumina, zeolites or molecular sieves. It may occur that during hydrogenation there is an isomerization and partial hydrocracking reaction, generally limited to a conversion lower than 15% by weight with respect to the total weight of the fraction fed. The small fraction of volatile compounds (150-°C) and water possibly formed can be optionally separated by means of distillation. The hydrogenated or non-hydrogenated light stream, according to the case, is then sent to a hydro-isomerization (HDSM) step through line 16, in which it is reacted, in the presence of hydrogen, under the usual conditions suitable for obtaining a widespread isomerization and a partial breaking of the linear hydrocarbon chains. Suitable conditions for the isomerization are listed in detail in the art, together with a large number of catalysts.

An aliquot, normally lower than 50%, preferably between 0 and 25% of said light fraction, can be possibly removed, through line 17, before the isomerization step, and mixed again with said heavy fraction of line 14 to be subjected to hydrocracking.

In said isomerization step, hydrogen is added to the hydrocarbon mix (line 15) in an amount of between 150 and 1500 normal-liters per liter of liquid and the mix is passed on a fixed bed of a suitable bi-functional catalyst

5   with a hydro-dehydrogenating activity, preferably consisting of an extruded product comprising from 30 to 70% by weight of amorphous micro/meso-porous silico-alumina, and from 0.2 to 1% by weight of platinum or palladium, with a space velocity of between 0.1 and 10 h^{-1}, at a temperature

10 ranging from 300 to 450°C and a pressure of between 1 and 10 MPa. The isomerization step is preferably effected so as to convert at least 60%, preferably at least 80% by weight of linear hydrocarbons into isomerized hydrocarbons, at the same time maintaining the amount of product having a boil-

15 ing point higher than 150°C converted to a product with a lower boiling point, below 30%, preferably 20% by weight, so as to limit the extension of the cracking.

The isomerized mix is sent, through line 24 to a fractionation column D3, after being joined to at least a part

20 of the light fraction 23 coming from the distillation column D2 of the heavy fraction subjected to hydrocracking. A middle distillate is obtained, according to the present invention, from column D3, possibly collected at two different levels in order to separate the kerosene (line 27) from

25 the gas oil (line 28), having excellent low temperature

properties, a high cetane number, preferably over 50, and a reduced emission of polluting agents.

In particular, it has been found that it is possible to obtain, by means of the present process, middle distil-
5   lates having the following characteristics:

	Kerosene (150 – 250°C)
Smoke point	> 50 mm
Flash point	> 40°C
Freezing point	< - 47°C
Aromatic compounds	< 0.1 %
Sulphur	< 0.1 ppm
	Gas oil (250 – 360°C)
B.C.N.	> 70
Flash point	> 160°C
Pour point	< - 12 °C
Aromatic compounds	< 0.1 %
Sulphur	< 0.1 ppm

Small amounts of low molecular weight products are ob-
20   tained from the distillation and fractionation column D3, particularly through line 25, a gaseous fraction C1-C5, of low interest, and, through line 26, a light fraction of hydrocarbon, preferably having a boiling point lower than 150°C (naphtha). According to a particularly advantageous
25   aspect of the present invention, the amount of said vola-

tile fractions is significantly reduced with respect to similar processes of the art, preferably to less than 20%, more preferably less than 15% by weight with respect to the initial feed of line 1.

5   The necessary amount of hydrogen (line 18) is added to the fraction (line 14) of high boiling hydrocarbons with a low oxygen content and unsaturated, and fed to the hydrocracking (HCK) unit according to step (i) of the present process, according to what has already been seen with re-

10   spect to the simplified scheme of Figure 1. The product obtained is sent, through line 19, to a distillation and fractionation apparatus D2, which is preferably run so as to obtain a separation of the hydrocarbon mix essentially into two fractions:

15 F1   a light fraction, with a boiling point lower than
           380°C, preferably lower than 360°C, preferably includ-
           ing less than 10% by weight of volatile products (150-
           °C) consisting of a product with a high iso-paraffin
           concentration, which is sent, through line 23, to the

20   same fractionation step of the light fraction 24 isom-
           erized in (HISM);

    F2   a residual fraction, consisting of a mix of isomerized
           high-boiling hydrocarbons, surprisingly having a re-
           duced content of waxes with respect to the products

25   obtained by means of other catalysts of the known art,

under similar conditions, whose initial boiling point is higher than 320°C, preferably higher than 340°C.

The combination of the two streams 23 and 24, coming from steps carried out with different feeds and under dif-
5   ferent conditions, but complementary, allows kerosene and gas oil fractions having the excellent properties listed above, to be advantageously obtained, after suitable dis-tillation in D3,. An aliquot, when necessary, preferably less than 50% by weight, of the mix F1 coming from distil-
10   lation D2, is sent, through line 29, to the same isomeriza-tion step (HISM), in order to further increase the degree and distribution of the isomerizations, and regulate the relative amount of the gas oil and kerosene produced.

The residual fraction F2 can be used as such for par-
15   ticular uses, or is preferably sent (line 20) to a dewaxing (DWX) step for producing lubricating bases. According to a preferred aspect, it is partially recycled to the hy-drocracking step (HCK) through line 22, for regulating the productivity of the process or varying the isomerization
20   degree according to the production demands.

The isomerization degree of the residual fraction sent to line 20 is preferably higher than 85%.

As the amount of linear paraffins is reduced, the de-waxing step, when necessary, can be advantageously ef-
25   fected, according to the process of the present invention,

under particularly favourable contact time and lubricating base yield conditions.

Said dewaxing step (DWX) can be effected according to the known techniques, both with a solvent and, preferably,

5   in the presence of a catalyst suitable for the purpose. In this latter case, the partially isomerised mix is again re-acted, in the presence of hydrogen and a suitable solid catalyst, preferably comprising a metal with a hydro-de-hydrogenating activity, usually a noble metal, supported on

10   a zeolite or other crystalline porous solid.

In this case, contrary to what takes place in solvent dewaxing, where the paraffin crystals are physically sepa-rated, the paraffins are selectively transformed into iso-paraffin compounds or lighter cracking products, according

15   to the catalyst used. The cracking products are mainly low molecular weight paraffins and olefins, partially (up to 50% by weight) consisting of C5- compounds, the remaining part being a material having a molecular weight within the gasoline range.

20   The catalytic materials mostly used are medium pore zeolites (such as mordenite, ZMS-5, SAPO-11) and, in some cases, larger pore materials (such as beta zeolites and HY), but also other materials have been proposed.

The catalytic dewaxing can be effected, according to

25   use, at pressures which can vary from 2 to 20 MPa, offering

higher operative pressures, advantages in terms of catalyst life cycle, higher yields and viscosity indexes of the de-waxed products. The preferred temperature conditions WABT and space velocity LHSV are those typical of hydrotreating,

5   the WABT ranging from 315 to 400°C and LSHV from 0.3 to 1.5 h^{-1}.

Downstream of the catalytic dewaxing, a treatment is normally envisaged on a typical "finishing" catalyst for improving the colour and removing any traces of reactive

10   molecules, such as olefins, in order to confer a better stability to the product.

At the end of said dewaxing step, after removing the last residues (< 3% by weight) of volatile products formed as a result of the partial hydrocracking, a liquid, isomer-

15   ized product is obtained (line 21) having excellent proper-ties at low temperatures and a high viscosity, having an initial boiling point of over 350°C, preferably > 360°C and with a distillation temperature (extrapolated) of 90% of the mix (T90) lower than 700°C (by extrapolation).

20   Some examples of practical embodiments are provided for a more detailed description of the present invention, which however are purely illustrative of some of the par-ticular aspects of the invention and should in no way be considered as limiting its overall protection scope.

25   EXAMPLES

The following analysis and characterization methods were used for running the practical embodiments of the present invention:

- X-ray diffractometry from powders (XRD): the analysis

5   was carried out using a vertical Philips X'PERT diffractometer equipped with a proportional pulsation meter and a secondary curved graphite crystal monochromator; two different measurements were effected for each sample: the first in the angular region $1.5 \leq 2\theta$

10   $\leq 10°$ with a step of $0.05°$ 2θ and accumulation times of 20s/step and fixed divergent slips of $1/6°$; the second within the spectral range of $3 \leq 2\theta \leq 53°$ with a step of $0.05°$ 2θ and accumulation times of 10s/step and fixed divergent slips of $1°$; in both cases the radia-

15   tion was CuKα (λ = 1.54178 Å).

- The information on the characteristics of the catalysts under examination are deduced from the evaluation of the adsorption/desorption isotherms of N_2 at the temperature of the liquid N_2, obtained by using a ASAP

20   2010 instrument (Micrometrics) and a Sorptomatic 1990. The samples (~ 0.3 g) have been degassed for 16 hours at 350°C at reduced pressure, before the acquisition of the isotherms.

- The total specific pore volume (V_P) was calculated us-

25   ing the Gurvitsch method at $p/p° = 0.995$. When the ad-

sorption isotherms end with a plateau, it is possible to exclude phenomena due to macropores or inter-particles porosity, therefore a precise determination of this parameter is possible. When the isotherms do not end with a plateau, V_p is only indicative.

- Measurement of the pore dimensions: the average pore diameter was determined by means of the DFT (density functional theory) method, of which details are provided in the publication of P.A. Webb and C. Orr, in "Analytical Methods in Fine Particle Technology", Micrometrics Instruments Corp. (1997), page 81.

- Measurement of the specific surface area: the specific surface area was evaluated by means of the BET linear graph with two parameters within the range of $p/p°$ 0.01-0.2 applying the DFT (density functional theory) method.

- Pour point: according to the regulation ASTM D97

- Viscosity at 100 cSt: according to the regulation ASTM D445

- Viscosity index: according to the regulation ASTM D2270

Reagents and materials

The commercial reagents listed below were used during the preparations described in the examples:

tetrapropyl ammonium hydroxide (TPA-OH)   SACHEM

aluminum tri-isopropoxide   FLUKA

tetra-ethyl silicate   DYNAMIT NOBEL

alumina (VERSAL 250, Pseudo-Bohemite)   LAROCHE

methyl cellulose (METHOCEL)   FLUKA

phosphoric acid   CARLO ERBA

5   The reagents and/or solvents used and not indicated

above are those most commonly used and can be easily found

at the normal commercial suppliers specialized in the

field.

Example 1: catalyst with P/Al = 1

10   239.50 ml of demineralized water, 3.40 g of an ammonia

solution at 30% by weight and 2.30 g of a solution of phos-

phoric acid at 85% by weight (equivalent to 0.02 moles of

tri-ammonium phosphate $(NH_3)_3PO_4$), are charged into a three-

necked flask, equipped with a rod stirrer and a bubble

15   cooler. 50.80 g of an aqueous solution at 40% by weight of

tetrapropyl ammonium hydroxide (TPA-OH, 0.01 moles) and

4.08 g of aluminum tri-isopropoxide (0.02 moles) are added

to the mixture thus prepared. The mixture is maintained un-

der stirring at room temperature for about 60 minutes, un-

20   til a limpid solution is obtained. 208 g of tetra-ethyl or-

thosilicate (TEOS; 1.00 moles) are rapidly added to this

solution and the temperature is brought to 60°C, the whole

mixture being maintained under stirring under these condi-

tions for a further 3 hours. At the end the formation of a

25   gel is observed, which is cooled to room temperature and

left to rest for 20 hours. In this way a homogeneous gel is obtained, characterized by the following molar ratios between the constituents: $Si/Al = 51$; $TPA-OH/Si = 0.098$; $H_2O/Si = 15$; $Si/P = 50$.

5   The gel thus obtained is first dried in air for about 3 hours and then calcined by heating, still in a stream of air, at 550°C for 5 hours. At the end, an amorphous solid is obtained according to the present invention, identified by the following empirical formula: $SiAl_{0.02}P_{0.02}O_{2.08}$.

10   The complete absence of crystalline aggregates was confirmed by means of X-ray diffraction. By means of NMR spectroscopy applied to the ^{31}P and ^{27}Al isotopes, it was found that at least 80% of the phosphorus is bonded by Al-O-P bonds to the amorphous silico-alumina matrix. The results

15   of the morphological analysis are summarized in Table 1 below.

EXAMPLES 2 and 3

       The procedure according to the previous example 1 was repeated modifying each time the quantity of tri-ammonium

20   phosphate initially produced by mixing ammonia and phosphoric acid in aqueous solution, so that the P/Al ratio in the gel ranges from 0.5 to 2 for Examples 2 and 3, respectively.

       The results of the morphological analysis and elemen-

25   tal analysis are summarized in Table 1 below.

Example 4

The procedure of Example 1 was repeated exactly, with the only difference that the hydrolysis and gelation step is carried out in an ethanol/water mixture in which the mo-

5   lar ratios ethanol/SiO_2 = 8 and H_2O/SiO_2 = 8. At the end the product thus obtained is subjected to characterization according to the above techniques. The morphological data are indicated in Table 1 below.

Example 5

10   239.50 ml of demineralized water, 6.78 g of an ammonia solution at 30% by weight and 4.59 g of a solution of phosphoric acid at 85% by weight (equivalent to 0.040 moles of tri-ammonium phosphate $(NH_3)_3PO_4$), are charged into a three-necked flask, equipped with a rod stirrer and a bubble

15   cooler. 50.8 g of an aqueous solution at 40% by weight of tetrapropyl ammonium hydroxide (TPA-OH, 0.10 moles) and 8.13 g of aluminum tri-isopropoxide (0.04 moles) are added to the mixture thus prepared. The mixture is maintained under stirring at room temperature for about 60 minutes, un-

20   til a limpid solution is obtained. 208 g of tetra-ethyl orthosilicate (TEOS; 1.00 moles) are rapidly added to this solution and the procedure is the same as in the previous example 1. At the end, an amorphous solid is obtained according to the present invention, identified by the follow-

25   ing empirical formula: $SiAl_{0.02}P_{0.02}O_{2.08}$. which is characterized

according to the above-mentioned techniques. The morphological data are shown in Table 1 below.

The structure of the solid catalysts obtained in accordance with the previous examples 2 to 5 was determined, as

5 for the product obtained in accordance with example 1, by means of X rays diffraction and NMR spectroscopy, and proved to be completely amorphous solids wherein at least 80% of phosphorus is bonded by means of Al-O-P links to the silico-alumina matrix.

10 Example 6 (comparative)

The procedure of Example 1 was repeated exactly, with the only difference that the P/Al ratio in the gel was equal to 5, instead of 1.

The structure of the solid thus obtained, determined

15 by means of X-ray diffraction and NMR spectroscopy, proved to be analogous to that of the product of Example 1, but the pore structure was greatly modified, with a partial collapse of the same, as shown by the significant reduction in their volume.

20 Example 7 (comparative)

An amorphous silica-alumina solid support was prepared not containing phosphorus, repeating the same procedure as the previous Example 1, but without introducing the solution of tri-ammonium phosphate. The results of the charac-

25 terization are summarized in Table 1 below. A significant

reduction in the average pore diameter is observed.

Table 1: Morphological properties of the catalysts

Example	Si/Al	P/Al	S_{BET} (m²/g)	Vp (ml/g)	d_{DFT} (nm)
1	50	1.0	700	0.96	6.1
2	·50	0.5	720	0.84	5.3
3	50	2.0	520	1.62	25.0
4	50	2.0	760	1.57	13.0
5	25	1.0	500	1.35	19.0
6 (comp.)	50	5	80	0.06	-
7 (comp.)	50	0	760	0.49	2.3

Example 8: extruded catalyst

5 kg of a humid gel prepared by exactly repeating the procedure of the previous Example 1, but omitting the drying and calcination step, 1.466 kg of alumina (pseudo-bohemite, VERSAL 150), previously dried for 3 hours in air at 150°C, and 0.205 kg of methyl cellulose are charged into a 10 litre plough mixer, maintained at a stirring rate of 70-80 revs per minute, and the mixture is left under stirring for about 1 hour. 50 ml of glacial acetic acid are then added and the temperature of the mixer is brought to about 60°C, continuing the stirring until a homogeneous paste is obtained, having the desired consistency for the subsequent extrusion. The mixture is charged into an extruder of the HUTT type, extruded and cut into cylindrical

pellets of the desired size (about 2 x 4 mm). The product
is left to rest for about 6-8 hours and then dried by main-
taining it in a stream of air at 100°C for 5 hours. It is
finally calcined in a muffle at 550°C for 5 hours in a
5   stream of air.

A porous extruded solid is thus obtained, with acidic
characteristics   (indicated   hereunder   with   the   term
"extruded product" for the sake of simplicity), essentially
consisting of an amorphous silica/alumina/phosphate phase
10   (60% by weight, by means of X-ray diffraction) and an alu-
mina crystalline phase (pseudo-bohemite), whose morphologi-
cal characteristics are specified in Table 2 below.

Examples 9, to 12 and 13 (comparative)

The same procedure was repeated as the previous Exam-
15   ple 8, but substituting the amorphous solid prepared ac-
cording to Example 1 with the solids prepared according to
the respective examples as indicated in the second column
of Table 2 below.

Porous extruded solids are thus obtained, whose mor-
20   phological characteristics are specified in Table 2.

25

Table 2: Morphological properties of the extruded products

Example	Amorphous phase (Example Nr.)	P/Al	S_{BET} (m^2/g)	Vp (ml/g)	d_{DFT} (nm)
8	1	1	540	0.91	7.6
9	3	2	460	1.26	18.0
10	4	2	510	1.25	16.0
11	2	0.5	n.d.	n.d.	n.d.
12	5	1	400	1.12	18.0
13 (comp)	7	0	590	0.88	< 6.0

EXAMPLE 14: formation of a hydrocracking catalyst based on platinum

In order to demonstrate the advantageous properties of the amorphous solid of the present invention as a catalytically active support in hydrotreatment processes of hydrocarbons, a hydrocracking catalyst was prepared, containing platinum as hydro-dehydrogenation metal.

In order to disperse the platinum on the support an aqueous solution of hexa-chloro platinic acid (H_2PtCl_6), hydrochloric acid and acetic acid was used in the following molar ratios: H_2PtCl_6/HCl/CH_3COOH = 1/0.84/0.05, having a platinum concentration of $7.69 \cdot 10^{-3}$ M. 60 ml of this solution were added to 30 g of the extruded solid, obtained according to the previous Example 8, so that the whole solid was covered by the solution, in order to avoid heterogene-

ity in the platinum distribution. The suspension thus ob-
tained was maintained under stirring for about an hour and
then degassed by suction under vacuum (about 1 kPa) at room
temperature. The solvent was subsequently removed by heat-
5   ing to about 70°C in a stream of air. The dry product was
finally calcined in a stream of air with the following tem-
perature profile 25-350°C in 2 hours, to 350°C for 2 hours,
350-400°C in 50 min., to 400°C for 3 hours.

At the end, a supported catalyst for hydrocracking is
10   obtained, having the following characteristics:

59.8% by weight of active amorphous solid (molar ratio
Si/Al = 51, P/Al = 1)

39.9% by weight of gamma-alumina

0.3% by weight of platinum

15   EXAMPLES 15, 16 and 17 (comparative)

A further three samples of hydrocracking catalyst were
prepared, exactly repeating the procedure of the previous
Example 14, but using the extruded products according to
Examples 9, 10 and 13 (comparative), in Examples 15, 16 and
20   17 (comparative), respectively. The composition character-
istics relating to amorphous phase, gamma-alumina and
platinum content of the catalysts obtained are essentially
the same as Example 14, whereas the morphological measure-
ments are specified in Table 3 below.

25   Table 3: morphological characteristics of the catalysts

with 0.3% Pt

Example	P/Al	S_{BET} (m^2/g)	Vp (ml/g)	d_{DFT} (nm)
14	1	490	0.84	7.3
15	2	430	1.12	15.0
16	2	470	1.02	16.0
17 (comp)	0	510	0.82	n.d.

EXAMPLE 18

120 ml of the aqueous solution of hexa chloroplatinic acid used in the previous examples (H_2PtCl_6/HCl/CH_3COOH = 1/0.84/0.05, [Pt] = 7.69•10^{-3} M), were added to 30 g of the extruded solid obtained according to the previous Example 8, so that the whole solid is covered by the solution, in order to avoid heterogeneity in the platinum distribution. The suspension thus obtained was treated with the same procedure described in the previous Example 14, to obtain at the end, after calcination, a supported catalyst for hydrocracking, having the following characteristics:

59.8% by weight of active amorphous solid (molar ratio Si/Al = 51, P/Al = 1)

39.9% by weight of gamma-alumina

0.59% by weight of platinum

Examples 19, 20 and 21 (comparative)

Three further samples of catalyst for hydrocracking

were prepared, containing 0.6% by weight of platinum, by exactly repeating the process of the previous example 18, but using the extruded products in accordance with the examples 11, 12 and 13(comparative), in the examples 19, 20

5   and 21(comparative), respectively. The composition characteristics relating to amorphous phase, gamma-alumina and platinum content of the catalysts obtained are essentially the same as Example 18, whereas the morphological characteristics do not significantly differ from those of the

10 original active support.

EXAMPLES 22 to 26

Various hydrocracking tests were carried out on a mix of paraffins, solid at room temperature, obtained through the Fischer-Tropsch synthesis, using the catalysts of the

15 previous Examples 18 to 21.

The hydrocracking tests were effected in a fixed bed tubular reactor having a useful charge volume of 15 ml, corresponding to a height of the catalytic bed in the isotherm section of about 10 cm. The reactor is equipped with

20 suitable connections for the continuous cocurrent feeding of the reagents and the removal of the reaction mixture. Hydrogen is fed at the desired pressure by means of a mass flow meter; the mixture of paraffins is maintained in the liquid state at a temperature of about 110°C and fed by

25 means of a pump.

The temperature of the reactor is controlled by means of a thermostat system capable of operating at up to 400°C. An adequate analytical instrumentation is connected on line for analysis in real time of the composition of the reac-

5   tion product.

8 g of catalyst are charged into the reactor and activated according to the method described above.

A 370+°C cut of a mixture of paraffins, obtained through a Fischer-Tropsch synthesis, having the following

10   composition, was used as feeding:

Fraction < 150°C	0.0
Kerosene (from 150 to 260°C)	0.3
Gas oil (from 260 to 370°C)	1.9
Fraction > 370°C	97.8

15

Various hydrocracking tests were carried out on said paraffinic composition, at a total pressure of about 5 MPa and a weight ratio hydrogen/(hydrocarbon mixture) of about 0.1. Table 4 below indicates the experimental conditions

20   and catalysts used in Examples 22 to 26. The contact time (1/WHSV) was regulated according to the usual technique in order to have the desired conversion degrees at the end.

25

Table 4: Process conditions

Conditions	Ex. 22	Ex. 23	Ex. 24	Ex. 25	Ex. 26(*)
Temperature (°C)	355	335	345	340	345
H_2/waxes (w/w)	0.105	0.105	0.105	0.105	0.105
Pressure (MPa)	5.0	5.0	5.0	5.0	5.0
Catalyst (Ex.Nr)	Ex. 18	Ex. 19	Ex. 20	Ex. 19	Ex. 21(*)
P/Al (atom/atom)	1	0.5	1	0.5	0
Si/Al (atom/atom)	51	51	25	51	51
WHSV (h^{-1})	2	2	2	2	2

(*) comparative

A fractionation was effected on the outgoing mixture by means of gas-chromatographic analysis, and on this basis, the conversion degree is measured of the hydrocarbon fraction having more than 22 carbon atoms $C_{22}+$, corresponding, more or less, to the fraction with a boiling point > 370°C. Table 5 below indicates the composition data relating to the yields in the various distillation cuts obtained at the end of the process.

An aliquot of the hydrocracking products is distilled at 360°C and the content of lubricating base is determined on the residue, according to the method explained herebelow. The 360+ residue is dissolved at 40°C in a 1/1 vol/vol mixture of methyl-ethyl ketone and toluene. The (solvent)/(360+ residue) ratio is 4/1 vol/vol; an aliquot of the solvent (about 1/8 of the total) is used in the washing

step of the paraffin collected on the filter. The tempera-
ture of the solution is lowered to -20°C at a rate of
1°C/min. At the end, the mixture is filtered at a tempera-
ture of -20°C. The de-waxed product is separated from the
5   solvent by distillation under vacuum and subsequent strip-
ping in a stream of nitrogen at 80°C.

The quantity of product obtained is measured to deter-
mine the content of lubricating base of said 360+ residue.
The lubricating base is then characterized by measuring the
10   viscosity at 100°C and the viscosity index. The results are
indicated in Table 5 below, which clearly demonstrates the
surprising improvements obtained with the catalytically ac-
tive support of the present invention, with respect to a
silica-alumina support having an analogous composition but
15   not containing phosphorus. In particular, according to Ex-
amples 22 to 25 in accordance with the present invention,
it is possible to obtain, by means of a single hydrocrack-
ing step, a high yield to middle distillates (columns 150-
260 and 260-370) and a high-boiling residue containing over
20   80% by weight of lubricating base having a much higher vis-
cosity than that obtained under the same process conditions
with a catalyst of the known art (comparative Example 26).

In addition to the above, other possible embodiments
or equivalent modifications of the present invention which
25   are not specifically mentioned herein, should be considered

as being simple variations of the same and, in any case, included within the scope of the following claims.

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Table 5: Composition and properties of the hydrocracking products.

Ex.	Temp. (°C)	WHSV (h^{-1})	Convers C_{22}^+	Yields to hydrocracking products (w%) (distillation ranges of fractions in °C)				Lubricating base		
				< 150	150-260	260-370	> 370	Yield % of 360+ residue	Viscosity at 100°C (cSt)	Viscosity index
22	335	2	80.27	23.4	24.180	32.2	19.3	99	5.23	143
23	335	2	63.8	17.1	22.714	23.972	36.034	96	5.97	157
24	345	2	69.6	22.6	20.332	26.808	30.189	87	5.47	145
25	340	2	73.3	19.7	23.657	30.416	26.137	100	5.34	148
26(*)	345	2	77.5	20.9	26.151	30.842	21.981	86	4.56	142

(*) Comparative